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3-BROMO-2-t-BUTYLSULFONYL-1-PROPENE. A VERSATILE MULTI-COUPLING REAGENT Part II [1]

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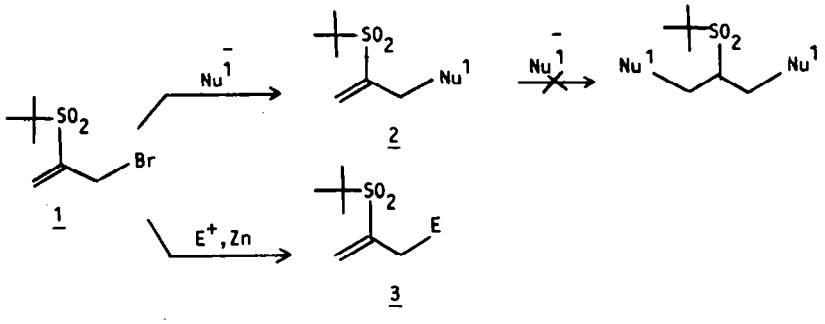
Summary - 3-Bromo-2-t-butylsulfonyl propene 1 is able to react with a large array of nucleophiles, but also of electrophiles in the presence of a metal[1]. We show here that the resulting functionalized vinyl sulfones can add a variety of nucleophiles like lithium organometallics, lithium cuprates, dimethyl malonate, or nitroalkanes, to furnish highly functionalized sulfones, in some cases with a high diastereoselectivity. The synthetic potential of 1 is illustrated by an approach to retinal structure and to various enones, and to a conjugated dienone.

A - Introduction

In the preceding paper of this series[1], we have shown that the title compound 1 may be used as an electrophilic or a nucleophilic species (Scheme 1)

Scheme 1



We have taken advantage of the fact that Nucleophiles Nu^1 react only once with the substrate 1[1], so that we could consider either 2 or 3 as potential candidates for a second nucleophilic addition (Scheme 2).

Scheme 2

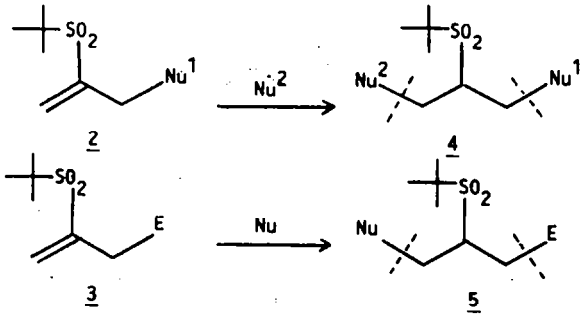
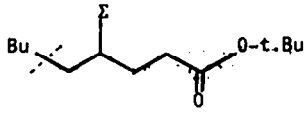
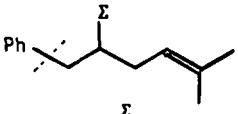
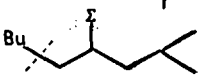
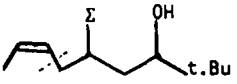
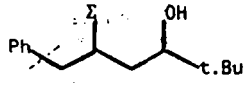
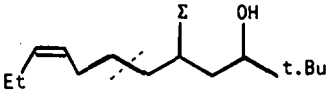
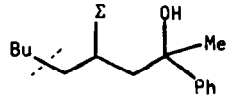
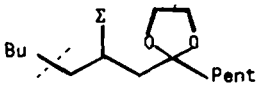
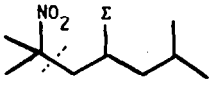
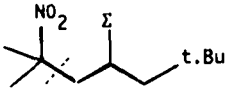
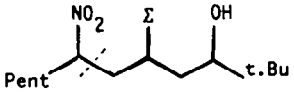
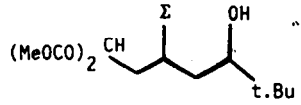
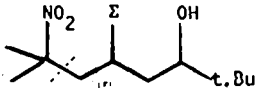
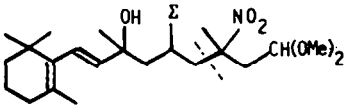


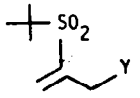
Table 1. Products of type 4 and 5 obtained by the addition of a nucleophile respectively to sulfones of type 2 and 3

Entry	Unsatur. sulfone	Nucleophile	Product of type 4 or 5[a,b]		Reaction conditions	Yield %
1	2a	Bu_2CuLi ($2^{eq.}$)	4a		1. hr at -35°	89
2	2b	$Ph_2CuLi.Me_2S$ ($2^{eq.}$)	4b		1. hr at -30°	72
3	2c	Bu_2CuLi ($2^{eq.}$)	4c		1.5hr at -30°	92
4	3a	(Z)-propen 1-yl lithium (2 eq.)	5a		0.30hr at -80°	81
5	3a	PhLi (2.1 eq.)	5b		0.30hr at -80°	93
6	3a	(Z)-3-hexenyl-lithium	5c		0.30hr at -80°	90
7	3b	BuLi (2.1 eq.)	5d		0.30 hr at -80°	88
8	3c	BuLi (1.05 eq.)	5f		1. hr at -80°	87
9	2c	2-nitropropane (excess)	4d		1eq. of DBU, 50 hr at 25°	75
10	2d	2-nitropropane (excess)	4e		1eq. of DBU, 12 hr at 120°	0
11	3a	1-nitrohexane (excess)	5g		1eq. of DBU, 1. hr at 25°	72
12	3a	dimethylmalonate	5h		1eq. of DBU, 19 hr at 25°	86
13	3a	2-nitropropane	5i		1eq. of DBU, 12 hr at 25°	90
14	3d	1,1-dimethoxy-3-nitrobutane 7 (excess)	5j		1eq. of DBU, 100hr at 25°	95

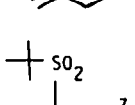
a/ The dotted lines in compounds 4 and 5 indicate the newly formed carbon-carbon bond
b/ The diastereoisomeric ratios determinated by ^1H NMR are : 5a:95/5, 5b:90/10, 5c:95/5, 5d:57/43, 5h:95/5, 5i:68/32.

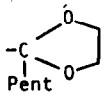
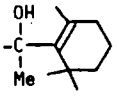
B - Results and discussion[3]

From our previous study[1] we selected compounds 2 a-c and 3 a-d :

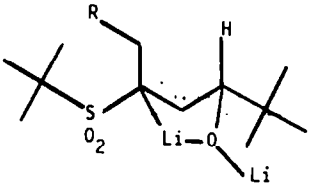


2a : Y = COO-ter-Bu, 2b : Y = CH=C(Me)$_2$,
2c : Y = i.Pr,



3a : Z = -CHOH-ter-Bu, 3b : Z = -C(Me)(Ph)(OH),
3c : Z =  , 3d : Z = 

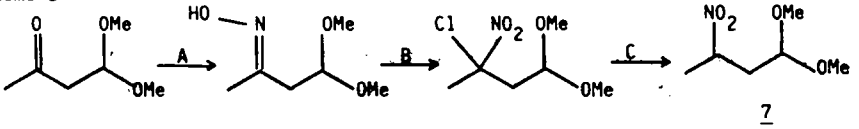
The various nucleophilic additions are quoted in table 1.
Thus, the addition of lithium cuprates[4] proceeds smoothly (within 1 hr at -30°) ; see entries 1-3 of table 1. The presence of an ester group in the unsaturated sulfone 2a is tolerated and the cuprate attacks selectively the vinyl sulfone functionality (see entry 1 of table 1). The β-hydroxy sulfone 3a reacts with various organolithium compounds (0.25 hr, -80°C) to give, after a remarkably diastereoselective protonation, the β-sulfonyl alcohols 5a-5c of a diastereoisomeric purity higher than 90% (see entries 4-6 of table 1). The formation of a chelate of type 6 :



6

may be responsible for the highly diastereoselective protonation. The two bulky groups (-SO$_2$tBu and -tBu) are both in pseudo-equatorial positions in 6. The utility of this control seems to be unfortunately limited, since the β-hydroxy sulfone 3b gives a mixture of diastereoisomers (see entry 7 of table 1).
A variety of nitroalkanes[5] and dimethylmalonate add to sulfones of type 2 and 3. Thus 1 equivalent of the unsaturated sulfone and 1 equivalent of 1,8-diazabicyclo (5.4.0) undec-7-ene (DBU) are stirred at 25° in the nitroalkane as solvent. The rate of the reaction depends greatly on the structure of the sulfone. The presence of a β-hydroxy group in the unsaturated sulfone leads to a fast reaction (compare for example entries 9 and 13 of table 1). The reaction is very sensitive to steric hindrance, since the sulfone 2d which differs from 2c by the presence of one more methyl group on β-position gives no addition reaction even under forcing conditions (12 hr at 120° ; compare entries 9 and 10 of table 1). Also a primary nitroalkane gives a faster reaction than a secondary one (compare entries 11 and 13 of table 1). Dimethylmalonate adds also under similar reaction conditions to furnish with good yield and high diastereoselectivity the highly functionalized sulfone 5h (entry 12 of table 1). The addition of the easily[6] available nitroalkane 7 (see scheme 3) leads in high yield to the hydroxy sulfone 5j which has the same carbon skeletton and the same oxidation state as retinal 8. This example demonstrates nicely the advantages of a synthesis strategy using a multi-coupling reagent, since the retinal precursor 5j was synthesized in only two steps starting from β-ionone, the nitro alkane 7 and the multi-coupling reagent 1 (see entry 14 of table 1 and scheme 4).

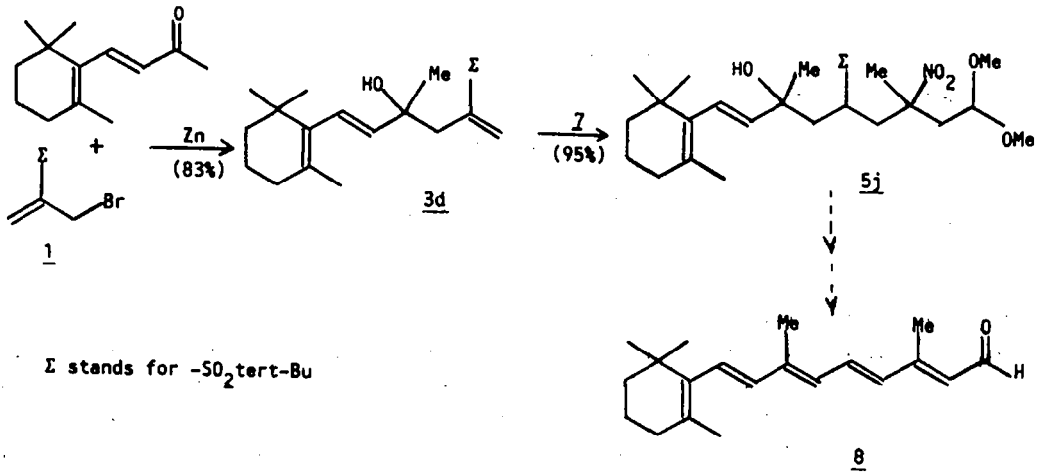
Scheme 3



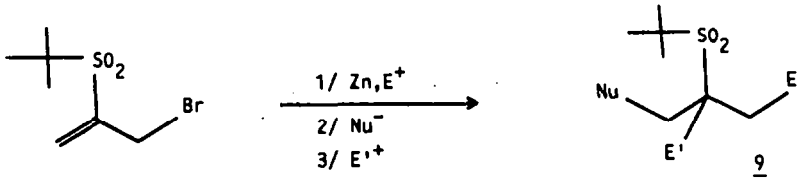
7

Reaction conditions : A : NH_3OHCl, AcONa, 60° (72%) ; B : HOCl (1 eq.) benzene then NaOCl (1 eq.), HSO_4 NBu_4 (54%) ; C : H_2, 1 atm., 25°, 4 hr, Pd/C (72%)

Scheme 4

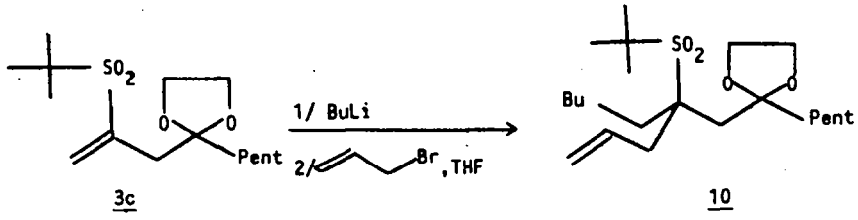


The starting sulfone 1 may be also looked at in terms of an $a^2d^2d^1$ synthon : if the α-sulfonyl carbanion is treated with an electrophile E' (instead of hydrolysis leading to 5).



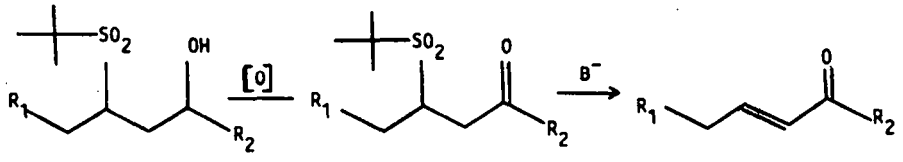
For example, alkylation of α-sulfonyl tertiary carbanions is well documented[7], and requires the use of polar aprotic solvents. We have checked that methylation was readily achieved in the presence of THF/HMPT : 80/20 and allylation occurs even in the absence of the latter solvent (Scheme 5)

Scheme 5



Finally, one example will be given, where the sulfonyl moiety of reagent 1 can be discarded, once the desired C-C couplings have been carried out. For example, in cases where a keto- or hydroxy group has been brought in, in β-position of the sulfone, a ready elimination leads to the enone (scheme 6)

Scheme 6

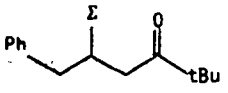
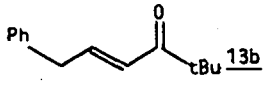
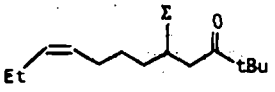
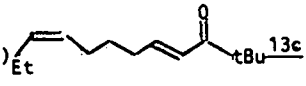
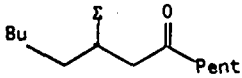
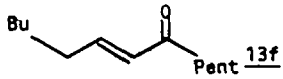
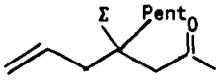
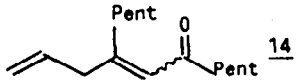


For this purpose, hydroxy derivatives 5b, 5c (see table 2) have been oxidized by pyridinium chlorochromate in dichloromethane[8] (1hr at 25°C) and ketals 5f, 10 have been hydrolyzed by

treatment with wet silicagel in dichloromethane 3hr at 25°C[9].

The ketones 11b, 11c, 11f, 12 thus obtained, when treated with one equivalent of DBU at 25°C in dichloromethane, lead respectively to enones 13b, 13c, 13f and 14 (see table 2).

Table 2. Preparation of enones and dienones from α-tert-butyl sulfonyl alcohols or acetals

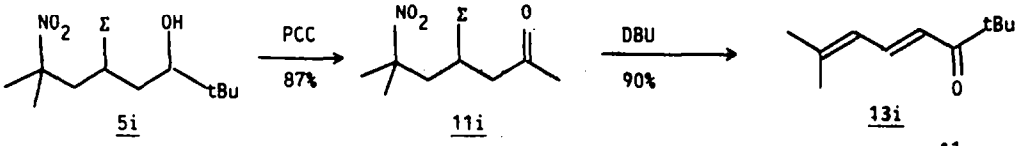
Substrate	Intermediate (Yield %)	Product	Yield %(a)
5b	 11b (87)	 13b	93
5c	 11c (88)	 13c	90
5f	 11f (85)	 13f	90
10	 12 (88)	 14	77

(a) from intermediate ketone

The newly formed C=C double bond is of E configuration (> 98%) except for enone 14 (E/Z=60/40).

δ-hydroxy-δ'-nitrosulfone 5i, once oxidized to the corresponding ketone 11i will eliminate sequencially one tert-butyl sulfonyl moiety, then a nitrite moiety, by treatment with excess of DBU (3hr at 25°C in dichloromethane) to give dienone 13i in 90% (E > 98% according to ^{13}C NMR). (See scheme 7)[10].

Scheme 7

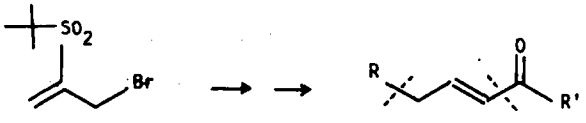


5i 11i 13i

Such a double elimination sequence has been recently used in a synthesis of coriolin[11].

C - Conclusion

The multicoupling ability of the bromovinylsulfone 1 allows the introduction of a variety of functional groups to prepare new vinyl sulfones of type 2, 3. These latter also add various nucleophiles giving highly functionalized substrates, hence a way, for example to enones or dienones:



EXPERIMENTAL PART -

THF and ether were distilled from sodium/benzophenone. Infrared spectra were recorded on a Perkin Elmer 457G spectrometer. Proton NMR spectra were obtained at 100MHz with a Jeol MH100 and at 250MHz with a Bruker AM 250. ^{13}C NMR spectra were obtained with a Jeol FX90. Chemical shifts in $CDCl_3$ solution are reported in ppm relative to tetramethylsilane as an internal standard. Gas chromatography was carried out with a Carlo Erba 2150 model equiped with a 12 OV 101 (20 m) column. Merck 60 (70-230 mesh) silica gel was used for the flash chromatography[12].

Addition of nucleophiles on sulfones of type 2 and 3

t-Butyl 4-t-butylsulfonylnonanoate 4a

A solution of lithium dibutylcuprate (8 mmoles) was prepared by the addition of 8.1 ml of BuLi (16 mmol) 1.98N in ether to a suspension of 1.55 g (8 mmol) of CuI in 32 ml of ether at -50°. After 15 min of stirring at -30°, 1.1 g (3.98 mmol) of the sulfone 2a dissolved in 3 ml of ether was added at -40°. After 1 hr at -35° the reaction was worked up as usually and the residue was purified by flash chromatography (solvent : hexane : CH_2Cl_2 : ether/20:20:1) to give 1.19 g of white crystals (m.p. 68°C ; 89% yield). See table 3 for the spectroscopic data.
Found : C, 61.10 ; H, 10.18%. Calcd. for $C_{17}H_{34}SO_4$: C, 61.04 ; H, 10.24%.

2-t-Butylsulfonyl-5-methyl-1-phenyl-4-hexene 4b

A solution of the complexe $Ph_2CuLi.Me_2S$ was prepared by the addition at -50° of 12 ml (10 mmol) of phenyllithium (0.83N in ether) to a suspension of 1.027 g (5 mmol) of $CuBr.Me_2S$ in 20 ml of ether. After 15 min of stirring at -20°, the now homogeneous solution of the cuprate was cooled to -40° and a solution of 550 mg (2.55 mmol) of the sulfone 2b was added. The reaction mixture was stirred 1 hr at -30° and worked up to give a residue which was purified by flash chromatography (solvent : hexane : ether : CH_2Cl_2/8:1:8). White crystals are obtained (540 mg ; 72% yield ; m.p. 49°). See table 6 for the spectroscopic data.
Found : C, 69.27 ; H, 8.96%. Calcd. for $C_{17}H_{26}SO_2$: C, 69.34 ; H, 8.90%.

2-Méthyl-4-t-Butyl sulfonyl nonane 4c

A solution of lithium dibutylcuprate (5 mmol) prepared as described above was cooled at -45° and a solution of 500 mg (2.45 mmol) of the sulfone 2c in 5 ml of ether was added. The reaction mixture was stirred 1.5 hr at -30° and worked up; The crude product was purified by flash chromatography (solvent : hexane : CH_2Cl_2 : ether/8:8:1) to give 590 mg of white crystals (m.p. 34° ; 92% yield). See table 6 for the spectroscopic data.

General procedure for the addition of organolithium compounds to sulfones 5 (a-d)

In a three neck-flask, fitted with a thermometer, a magnetic bar and a septum, and flushed with argon, 2.5 mmol of the vinyl sulfone in 8 ml THF are first added. The mixture is cooled to -80°C and a solution of the lithium compound (2.1 eq.) is added dropwise in 10 min, with a syringe, or with a teflon cannula. The reaction is followed by t.l.c. and is over in 30-40 min at -80°C. 20 ml of sat. aqueous NH_4Cl solution and 20 ml CH_2Cl_2 are then added. The two phases are separated The aqueous layer is extracted (20 ml CH_2Cl_2). The organic phases are joined, then washed to neutral with small portions of HCl 1N, then 10 ml of brine. After drying over magnesium sulfate, and evaporation of the solvents under a vacuum, the crude product is flash chromatographed. See table 3 for NMR data.

5-tert-Butylsulfonyl-2,2-dimethyl-7-nonen-3-ol (Z) 5a

(from (Z)-propen-1-yl lithium and 3a). Obtained : 0.58 g (81%)
Eluent CH_2Cl_2 : hexane : ether/70:30:5. m.p. : 85°C (CH_2Cl_2/pentane). Only one diastereoisomer is found by NMR (d.r > 95/5).
Found : C, 61.98 ; H, 10.51%. Calcd. for $C_{15}H_{30}SO_3$: C, 61.98 ; H, 10.51%.

5-tert-Butylsulfonyl-6-phenyl-2,2-dimethyl-3-hexanol 5b

(from phenyllithium and 3a). Found 0.76 g (93%).
Eluent : CH_2Cl_2 : hexane : ether/70:30:10.
Oil. The two diastereoisomers (90/10) are not separated

5-tert-Butylsulfonyl-2,2-dimethyl-9 dodecen-3-ol (Z) 5c

(from (Z)-3 hexenyllithium and 3a). Obtained : 0.75 g (90%). Eluent same as for 5b
Oil. Only one diastereoisomer is detected by NMR.

4-tert-Butylsulfonyl-2-phenyl nonan-2-ol 5d

(from n.Butyllithium and 3b). Obtained : 0.74 g (88%). Eluent : same as for 5a.
Oil. The mixture of the two diastereoisomers (57/43) is not separated.
Found : C, 67.06 ; H, 9.50%. Calcd for $C_{19}H_{32}SO_3$: C, 67.02 ; H, 9.47%.

Preparation of the dioxolane 3c[13]

Prepared according to R. Noyori
In a three-neck flask equipped with a thermometer and a magnetic bar, are placed 350 mg (1.34 mmol) of 2-t-Butylsulfonylnon-1-en-4-one, 350 mg (1.7 mmol) of 1,2-bistrimethylsilyoxy ethane, and 2 ml CH_2Cl_2. The mixture is cooled at -78°C and one drop on trimethylsilyltrifluoromethane sulfonate is added. After stirring at -40°C for 24 h, the mixture is hydrolyzed with 5 ml of a saturated sodium hydrogencarbonate solution; The organic phase is washed with 2 x 20 ml of sat. $HNaCO_3$ solution, 20 ml water, and 20 ml brine. After drying of the organic phase on magnesium sulfate and evaporation of solvents, 401 mg (99%) of pure 3c are obtained.

Dioxolane of 6-tert-butylsulfonyl-8-tridecanone 5f
From 3c, see general procedure but 1.05 eq. of n.BuLi is used instead of 2.1 eq.
0.4 g (87%) of 5f (oil) are obtained. Same eluent as for 5a. (NMR data, table 3)

General procedure for the addition of nitroalkanes or malonates
In a flask equipped with magnetic stirring are placed 1.2 mmol of the vinylic sulfone, 1.5 ml of nitroalkane or dimethyl malonate and 220 mg (1.45 mmol of 1,5-diazabicyclo(5,4,0)undene-5 (DBU)) under an argon atmosphere. The reaction is followed by t.l.c. When the reaction is over, 100 ml of CH_2Cl_2 are added, and the organic layer is washed successively with a 10% HCl solution (3 x 30 ml), a saturated solution of sodium carbonate (30 ml) and brine (30 ml). After drying over magnesium sulfate, and evaporation of solvents under vacuum, the crude product is purified by chromatography [10]. The reaction conditions (time, temperature) are quoted in table 1 ; spectroscopic data are quoted in table 3.

4-tert-Butylsulfonyl-2-nitro-2,6-dimethylheptane 4d
From 2c, and 2-nitropropane, 0.18 g of 4d are obtained (75%) as an oil. Same eluent as for 5a.

5-tert-Butylsulfonyl-7-nitro-2,2-dimethyl-3-dodecanol 5g
From 3a and 1-nitrohexane, 0.32 g (72%) of 5h (oil) are obtained (same eluent as for 5b. Four diastereoisomers are obtained, and not separated.

Dimethyl-(2-tert-butylsulfonyl-4-hydroxy-5,5-dimethyl-1-hexyl)-2-malonate 5h
From 3a and dimethylmalonate, 0.39 g of 5i are obtained (86%) as an oil ; same eluent as for 5b. Only one diastereoisomer is observed in NMR.

5-tert-Butylsulfonyl-7-nitro-2,2,7-trimethyl-3-octanol 5i
From 7c and 2-nitropropane, 0.37 g of 5i are obtained (90%). Same eluent as for 5b. Crystals. m.p. : 123°-132°C (from CH_2Cl_2/Pentane). Mixture of two diastereoisomers (68/32).
Found : C, 53.25 ; H, 9.30%. Calcd. for $C_{15}H_{31}NSO_5$: C, 53.39 ; H, 9.26%.

1,1-Dimethoxy-3-nitrobutane 7 [6]
1/ In a flask containing 60 ml of water kept at 60°C and stirred magnetically, are added 20 g of 1,1-dimethoxybutan-3-one (150 mmol), 2 g of sodium acetate (24.3 mmol) and 16 g of hydroxylamin hydrochloride (230 mmol). The mixture is stirred for 45 min, while the temperature is allowed to reach 25°C, and then extracted with ether (4 x 50 ml) ; the organic phases are joined and washed with a saturated solution of sodium hydrogencarbonate, until neutral, then with brine. The solution is dried over potassium carbonate and solvents are evaporated under vacuum. The yellow oil is distilled (b.p. 126°C/10 torr) ; 16 g (72%) of the oxime is thus obtained.
2/ To 61 mmol (9 g) of the oxime, in 300 ml of benzene, is added 1 equivalent (332 ml) of hypochlorous acid 0.184N at P_H5.5, obtained by acidification by sulfuric acid, of a commercial solution of sodium hypochlorite. The two-phase blue solution is vigorously stirred for 30 min at 25°C. The organic phase, containing the chloronitroso intermediate is treated with 245 ml of a solution of sodium hypochlorite at P_H10.0, containing 7.06 g of tetrabutylammonium hydrogenosulfate. After stirring for 30 min at room temperature, the blue colour is discharged, the organic phase is decanted, and the aqueous phase is extracted with ether (4 x 50 ml). The joined organic phases are washed with brine (2 x 100 ml), then dried over magnesium sulfate, and solvents are evaporated under vacuum.
The crude oil is then purified by bulb to bulb distillation to give 16 g (54%) of 1,1-dimethoxy-3-chloro-3-nitro butane b.p.= 65°C/1 torr.
Note : P_H values must be controlled accurately (± 0.1 unit), and the commercially available "line water" must be of recent origin.
3/ 2.7 g (13.6 mmol) of the preceding chloro nitro acetal are dissolved in a mixture of methanol (150 ml) and NaOH 2N (36 ml). 495 mg of palladium 5% on charcoal are added, and hydrogenation is performed under a normal pressure of H_2 at 23°C for 4 h. After filtration of the catalyst, and addition of 17 ml of acetic acid, the mixture is continuously extracted with pentane during 12 h. Pentane is distilled under normal pressure and the residue is distilled to give 1.61 g (72.2%) of nitroacetal 7 b.p. = 88°C/3 torr.

5-tert-butylsulfonyl-3-nitro-1,1-dimethoxy-3,7-dimethyl-9-(2,6,6-trimethylcyclohexen-1-yl)-2 nonen-7-ol 5j
see the general procedure starting from 3d and 7.
4.12 g (95%) of 5j are obtained as an oil (same eluent as for 5b) containing 4 diastereoisomers.

Alkylation

Dioxolane of 4-tert-butylsulfonyl-4-n.pentyl-1-undecene-6-one (10)
3c is treated according to the procedure leading to 5f, but instead of hydrolyzing the reaction mixture, 4 mmol (0.49 g) of allyl bromide in 5 ml THF are added, and the temperature is allowed to raise to 25°. The reaction is followed by t.l.c. until completion, and the mixture is hydrolyzed according to the general procedure leading to 5a-d.
0.64 g of dioxolane 10 (80%) are obtained, as an oil.

Synthesis of enones and dienones
General procedure for the oxidation of alcohols into ketones
To a solution of 2.3 mmol of the alcohol in 10 ml CH_2Cl_2 is added 1.6 g (7.4 mmol) of pyridinium chlorochromate, and the mixture is magnetically stirred over 8 hr at room temperature. The

mixture turns black and a precipitate separates out. 50 ml ether and 50 ml dichloromethane are added, and the mixture is filtrated over a short column of silicagel (3 x 3 cm) deposited on a sintered glass to remove the chromium salts.
The precipitate is washed with CH_2Cl_2 until the filtrate is free of product. The filtrates are joined and solvents are evaporated in vacuum. The residue is purified by flash chromatography on silicagel. For spectroscopic data see table 4.

5-tert-Butylsulfonyl-6-phenyl-2,2-dimethyl-3-hexanone 11b
From 5b. Eluent CH_2Cl_2:hexane:ether/70:30:5. Obtained 0.65 g (87%) of 11b (oil).

5-tert-butylsulfonyl-2,2-dimethyl-9-dodecen-3-one (Z) 11c
From 5c. Same eluent as above. Obtained 0.67 g of 11c as an oil

5-tert-Butylsulfonyl-7-nitro-2,2,7-trimethyloctan-3-one 11i
From 5i. Same eluent as above. Obtained 0.67 g of 11i as an oil.

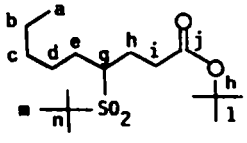
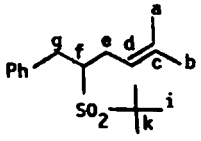
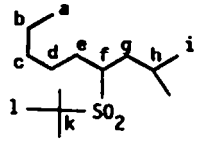
General procedure for the hydrolysis of sulfo-acetals
Silicagel for chromatography (3 g) is added, with stirring, to 4 ml CH_2Cl_2, in order to obtain a homogeneous paste. 20 drops of 10% sulfuric acid are then added, followed by 1 mmol of the acetal in 1 ml of dichloromethane. The mixture is stirred for 4 hr at room temperature and 500 mg of solid hydrogen sodium carbonate are added. Stirring is continued for 10 min and the mixture is filtered. The precipitate is washed with dichloromethane (50 ml) and ether (50 ml). The joined solutions are evaporated under vacuum, and the residue is chromatographed on silicagel. Spectroscopic data in table 4.

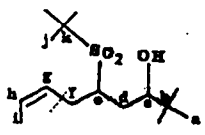
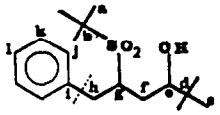
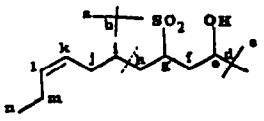
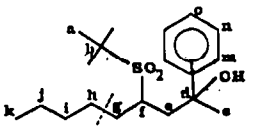
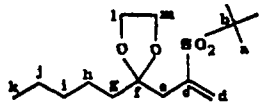
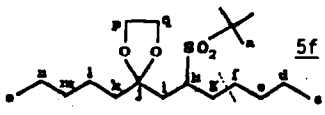
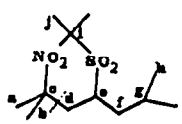
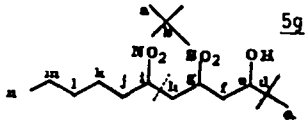
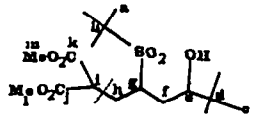
8-tert-Butyl-6-tridecanone 11f
From 5f. Same eluent as above. 0.202 g of 11f (85%) are obtained as an oil.
Found : C, 64.06 ; H, 10.86%. Calcd. for $C_{17}H_{34}SO_3$: C, 64.10 ; H, 10.76%.
4-tert-Butylsulfonyl-4-n.pentyl-1-undecen-6-one 12
From 10. Same eluent as above. 0.315 g of 12 (88%) are obtained as an oil.

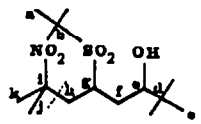
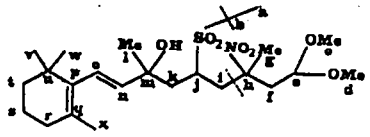
General procedure for the elimination reactions by DBU
2.1 mmol of DBU (294 mg) (4.2 mmol in the case of nitroketone 11i) are added to a solution of 2 mmol of the ketone in 10 ml dichloromethane. The mixture is stirred at room temperature. The reaction is followed by t.l.c. When it is over (30 min to 90 min), 100 ml of dichloromethane are added, and the solution is washed successively with a 10% HCl solution (3 x 20 ml), a sat. solution of hydrogen sodium carbonate (2 x 20 ml) and brine (20 ml). The organic phase is dried over magnesium sulfate and then evaporated, and the residue is chromatographed on silicagel.

6-Phenyl-2,2-dimethyl-4-hexen-3-one (E) 13b
From 11b. Eluent:CH_2Cl_2:hexane:ether/70:30:1. 375 mg (93%) of ketone 13b are obtained as an oil.
Found : C, 83.05 ; H, 9.05%. Calcd. for $C_{14}H_{18}O$: C, 83.12 ; H, 9.00%.
2,2-Dimethyl-4,9-dodecadien-3-one (4E,9Z) 13c
From 11c. Eluent : CH_2Cl_2:hexane/70:30. 381.6 mg of 13c are obtained as an oil (90%).
7-Tridecen-6-one (Z) 13f
From 11f. Same eluent as in the preceding example. 353 mg of ketone 13f are obtained as an oil.(90%).
4-n.Pentyl-1,4-undecadien-6-one 14
From 12. Same eluent as in the preceding case. 364 mg of ketone 14 are obtained as an oil (77%). Mixture of two isomers E/Z = 40/60.
2,2,7-Trimethyl-4,6-octadien-3-one (E) 13i
From 11i. Eluent : pentane:CH_2Cl_2/40:60. 299 mg of ketone 13i are obtained as an oil. (90%).

Table 3. Spectroscopic data of compounds 4a-4e and 5a-5j

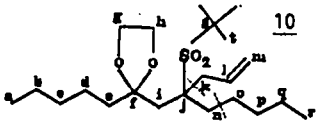
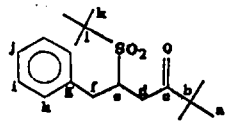
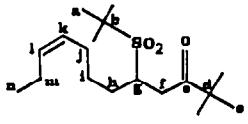
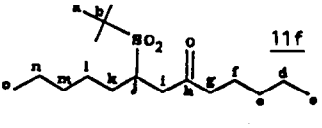
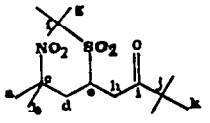
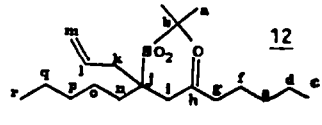
Structure		^1H Spectra[a]	^{13}C NMR Spectra[a]	I.R.[b]
	4a	0.94(t,J=6.6Hz,3H,(a)); 1.27-2.35m,10H,(b,c,d, e,h);1.46(s,9H,(m));1.50 (s,9H,(l));2.50(m,2H, (i));3.36(m,1H,(g))	172.1(j);80.5(k);60.8(n) 32.1;31.7;28.8;28.1(l) 26.5;24.3;23.8(m);22.4; 14.0(a)	2950,2920,2980, 1732,1468,1425, 1380,1362,1321, 1270,1150,1100, 849,700
	4b	1.43(s,9H,(i));1.48(s, 3H,(a));1.70(s,3H,(b)); 2.55(m,2H,(e));3.02(m, 1H,(g));3.35(m,1H,(g)); 3.53(m,1H,(f));5.28(t, J=6Hz,1H,(d));7.40(m,5H, arom. H)	138.2;134.5;129.1;128.5 126.7;120.0;60.8(h);59.3 (f);34.9(g);27.7(e);25.7 (b);23.8(i);17.7(a)	3060,3020,2960, 2920,1600,1490, 1465,1450,1285, 1110,800,748,700
	4c	0.93(m,9H,(i,j,a));1.27- 2.08(m,11H,(b,c,d,e,g, h));1.46(s,9H,(l));3.26 (m,1H,(f))	60.8(g);55.7(f);38.0; 31.9;29.5;26.4;26.0;24.1; 23.1(l);22.4(j);21.8(i); 14.0(a)	2960,2940,2870, 1465,1370,1285, 1120,1105,800, 700

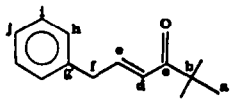
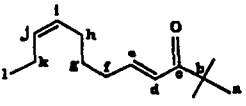
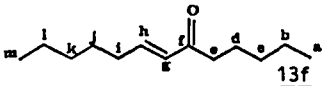
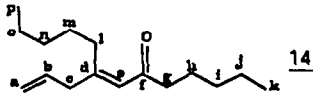
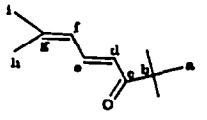
	5a	0.94(s,9H,(a));1.50(s, 9H,(j));1.70(d,3H, J=6.5Hz,(i));1.90(m,2H, (f));2.75(m,2H,(d));3.34 (m,1H,(e));3.76(la,2H, (OH,c));5.70(,m,2H,(h,g))	126.81;125.65;76.72(c); 61.38(k);54.37(e);35.04 (d);30.78(b);26.39(f); 25.53(a);23.95(j);12.96 (i)	c
	5b	0.72(s,9H,(c));1.40(s, 9H,(a));1.60-2.20(m,2H, (h));2.86(m,2H,(f)); 2.95-3.55(m,2H,(e,g)); 3.88(la,1H,OH);7.50(s, 5H,phenyl)	major isomer:137.5(i); 129.49;128.38;126.63(f) 76.90(e);61.32(b);56.37 (g);35.28(f);34.83(h); 31.25(d);25.33(c);23.84 (a)	3515,3085,3060, 3030,2960,2910, 2870,1600,1495, 1480,1455,1395, 1365,1280,1220, 1195,1110,1070, 1005,960,910,865, 845,800,735,700, 660
	5c	0.90(m,12H,(c,n));1.40 (s,9H,(a));1.58-2.20(m, 10H);3.00(m,1H,OH);3.30 (m,1H);3.65(m,1H);5.48 (m,2H,(k,l))	132.23;128.09;76.72(e); 61.13(b);54.67(g);35.04 (f);31.25(d);28.30(h); 27.02;26.55;25.56(c); 23.95(a);20.46(i);14.27 (n)	3510,2960,2870, 1655,1480,1465, 1400,1365,1280, 1215,1200,1115, 1070,1010,965,945, 920,850,835,805, 740,705,655
	5d	0.90(m,(k));1.32and 1.40 (2s,9H,(a));1.54and 1.62 (2s,3H),(c));2.00(m,2H, (g));2.70(,m,2H,(e)); 3.30(m,1H,(f));3.60 and 4.14(2s,1H,OH);7.50(m, 5H,(phenyl))	148.32(l);146.17(l); 128.12;126.66;125.23; 124.60;73.09(d);72.85(d); 61.62(b);61.35(b);54.41 (f);53.75(f);42.37;41.68; 32.21;31.79;31.52;31.14 29.41;26.58;25.47;24.07 (a);23.95(a);22.37;14.03 (k);13.76(k)	3470,3080,3060, 3020,2960,2930, 2870,1600,1490, 1480,1460,1445, 1395,1370,1275, 1145,1105,1070, 1030,940,915,800, 770,705,655
	3c	0.90(t,3H,J=6.5Hz,(k)); 1.40(s,9H,(a);la,8H); 2.82(s,2H,(e));4.06(s, 4H,(l,m);6.43(s,1H, (Hd trans/SO_2));6.54(s, 1H,(Hd cis/SO_2))	142.48(c);131.87(d); 110,95(f);65.04(l,m) 59.88(b);37.54(e);36.86 (g);31.91;23.53(a);22.88; 22.55;14.00(k)	2950,2925,2870, 1620,1480,1465, 1430,1395,1380, 1365,1290,1195, 1115,1100,1080, 1030,950,925,895, 875,825,805,745, 685,665
	5f	0.90(t,6H,J=6.5Hz,(c,o)) 1.30-1.50(la,16H);1.40 (s,9H,(a));2.24(m,2H,(i), part of an ABX system; 4.04(s,4H,(p,q);3.44(m, 1H,(h),part of an ABX system	110.95(j);64.80(p or q); 61.08(b);52.76(h);37.81 (i);35.87(k);31.94;30.63; 26.64;23.89(a);22.37; 14.00(c,o)	2955,2930,2870, 1480,1465,1380, 1365,1285,1200, 1110,1085,1035, 950,820,805,695, 660
	4d	0.96(m,6H,(h));1.2-1.8 (m,3H,(f,g));1.47(s,9H, (j));1.71(s,6H,(a,b)); 2.08(dxd,part of an ABX system,JAB=16.5Hz,JAX= 6Hz,1H,(d);2.82(dxd,part of an ABX system,JAB= 16.5Hz,JAX=6Hz,1H,(d)); 3.36(m,1H,part of an ABX system,(e))	87.45(c);61.83(i);52.26 (e);41.15 and 40.46(a,b); 27.29;25.39(h);24.25(j); 22.97;21.87	c
	5g	0.90(m,12H,(c,h));1.30 (la,6H,(k,l,m));1.48(s, 9H,(a));1.80(la,3H); 2.40(la,3H);3.30(la,3H); 4.75(la,1H,OH)	86.14 and 85.51(i);76.96 (e);62.15 and 61.28(b); 52.17 and 51.18(g);35.34; 35.01;34.56;25.41(c); 23.95 and 23.68(a);22.28; 13.88(n)	c
	5h	0.94(s,9H,(c));1.45(s, 9H,(a));1.65-2.6(m,6H); 3.40(la,1H,(g));3.80(s, 6H,(l,m));4.00(m,1H,OH)	170.07 and 169.15(j,k); 76.01(e);61.23(b);52.76 (g);51.93(i);49.73(h); 34.95(f);32.89(d);27.77; 25.59(c);23.81(a)	c

	5i	0.88(s,9H,(c));1.40 and 1.44(2s,9H,(a));1.67(s, 6H,(j,k));1.90-2.50(m, 3H);2.50-3.30(m,2H); 3.74(m,1H,OH)	88.05 and 87.12(i);75.95 (e);62.15 and 61.49(b); 51.07(g);40.19(h);34.89 (f);34.20;25.38(c);24.34 and 23.81(a)	3495,2960,2870, 1535,1470,1400, 1375,1365,1345, 1320,1300,1270, 1215,1190,1150, 1135,1105,1070, 1010,990,960,940, 915,885,800,730, 715,660,625
	5j	1.04(s,6H,(v,w));1.32 and 1.35(2s,3H,(g));1.45(s, 9H,(a));1.72(s,3H,(x)); 1.76(s,3H,(l));1.80-3.20 (m,12H);3.34(s,6H,(c,d)); 3.80(m,1H,(f));4.50(t,1H, J=6.5Hz,(e));5.56 and 6.30(2m,2H,(n,o))	138.64(p);136.40(n); 128.92(q);126.39(o); 101.27 and 101.09(e); 87.81 and 87.56(h); 71.95(m);63.02(b); 54.24(c,d);52.76(j); 34.06;28.78;24.55(a); 21.54(x)	c

a/ All spectra in $CDCl_3$, TMS as internal standard ;
b/ I.R. spectra are recorded as films (liquids) or KBr plates (solids) ;
c/ not recorded

Table 4. Spectroscopic data of compounds 10 (alkylation), 11 (ketosulfones), 13 and 14 (enones)

Structure		^{1}H NMR Spectra[a]	^{13}C NMR Spectra[a]	I.R.
	10	0.92(m,6H,(a,r));1.58 (s,9H,(t));1.10-1.80(m, 14H,(b,c,d,n,o,p,q); 1.98(m,2H,(e));2.55(s, 2H,(i));2.91(m,2H,(k)); 4.05(m,4H,(g,h));5.19 (m,2H,(m));6.18(m,1H,(i))	134.40;117.66;11.73(f); 75.59(g,h);67.07(j); 63.61(s);39.09;38.79; 36.92;34.71;32.63;31.97; 26.19(t);23.84;22.56; 14.06(a,r)	3070,2960,2930, 2870,1635,1460, 1360,1275,1100, 1030,945,912,700, 680,650
	11b	1.04(s,9H,(a));1.45(s, 9H,(k));2.40-3.10(m,2H, (f));3.40(m,2H,(d)); 4.50(m,1H,(e));7.40(s, 5H,(phenyl))	211.58(c);136.76(g); 129.16 and 128.68(h,i); 126.99(j);61.17(l);52.26 (e);43.86(b);36.29;35.69; 26.37(a);23.71(k)	c
	11c	0.96(t,3H,J=7.5Hz,(n)); 1.16(s,9H,(c));1.38(s, 9H,(a));2.04(m,4H(m,n)); 2.68(dxd,1H,part of an ABX system,JAB=18Hz, JAX=6Hz,(f);3.40(dxd,1H part of an ABX system, JAB=18Hz,JAX=6Hz,(f); 4.08(m,1H, part of an ABX system,(g);5.42(m, 2H,(k,l)	211.57(e);132.53(k); 127.82 ; 60.69(b);51.52 (g);44.09(f);36.38(h); 30.21;26.90,26.57(c); 23.68(a);20.50;14.27(n)	2960,2940,2880, 1710,1480,1465, 1400,1370,1350, 1285,1200,1115, 1065,1010,940,915, 850,805,715,700, 660
	11f	0.90(m,6H,(c,o));1.44(s, 9H,(a));1.10-2.00(la, 14H,(d,e,f,k,l,m,n)); 2.50(m,3H,(g,i));3.20 (m,1H,(i));4.00(m,1H,(j))	207.16(h);60.72(b);52.23 (j);42.94(l);41.33(g); 31.52;31.31;30.66;26.64; 23.67(a);23.30;22.43; 13.91(c,o)	c
	11i	1.20(s,9H,(k));1.44(s, 9H,(g));1.68(d,5H,J=3Hz (a,b));2.25-2.85(m,3H, (d,h));3.57(dxd,1H,part of an ABX system,JAB=21Hz JAX=6.5Hz,(d));4.26(m,1H, part of ABX system,(e))	211.04(i);86.77(c);61.92 (f);47.76;43.83;40.37; 38.22;26.58(g);23.75(k)	c
	12	206.75(h);133.72(l); 128.82(m);75.20(j);66.65 (b);44.54(i);42.78(g); 39.09(k);34.77(n);32.29; 31.22;25.95(a);23.98; 23.30;22.46;14.03;13.91	c	c

 13b	1.12(s,9H),(a));3.20(m, 2H,(f));6.45(m,2H,(d,e)) 7.36(m,5H,(phenyl)	212.79(c);137.06(g);132.59 (e);128.36(i);127.16(j); 126.09(h);123.32(d);44.12 (b);40.31(f);26.19(a)		c
 13c	0.96(t,3H,J=7.5Hz,(l)); 1.20(s,9H,(a));1.52(m, 2H,(g));2.12(m,6H,(f,h, k));5.40(m,2H,(i,j)); 6.60(m,1H,(d));7.06(m, 1H,(e))	203.41(c);147.01(e);132.29 (i);128.18(j);124.33(d); 42.70(b);31.91;28.30;26.54; 26.19(a);20.56;14.36(l)		c
 13f	0.96(m,6H,(a,k));1.40 (lm,14H);2.24(m,2H,(i); 2.56(t,2H,J=7.5Hz,(e)); 6.10(m,1H,(g));6.90(m, 1H,(h))	200.76(f);147.18(h);130.38 (g);40.04(e);32.47;31.58; 31.43;27.88;24.07;22.52; 13.97(a,m)		c
 14	0.90(m,6H,(k,p));1.10- 2.00(1a,12H);2.20(m,2H, (l));2.28(t,2H,J=6.5Hz, (g));3.16 et 3.30(2s,2H, (c));5.20(m,2H,(a));6.06 (m,1H,(b));6.64(m,1H,(e))	208.36 and 207.49(f);136.88; 136.16;132.61;129.99; 128.62;116.71;116.53;51.60; 45.56;41.80;37.99;31.79; 31.64;31.46;30.93;28.04; 27.50;24.16;23.51;14.03;13.99		c
 13i	1.16(s,9H,(a));1.92(ls, 6H,(h,i));6.10(d,1H, J=12Hz,(d));6.56(d,1H, J=16Hz,(f);7.72(dxd,1H, J_1=12Hz,J_2=16Hz,(e))	204.72(c);147.04(e); 139.17;124.39(d);121.75; 42.81(b);26.37(a);18.95 (h,i))	2965,2930,2870, 1680,1630,1590, 1480,1450,1395, 1385,1365,1355, 1310,1285,1250, 1075,1005,885,780	

a/ $CDCl_3$ as solvent and TMS as internal standard ;
b/ recorded as films (liquids) or KBr plates (solids) ;
c/ not recorded

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